

REMOVAL OF HEXAVALENT CHROMIUM FROM DRINKING WATER BY GRANULAR FERRIC HYDROXIDE

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ABSTRACT

Removal of chromium can be accomplished by various methods but none of them is cost-effective in meeting drinking water standards. For this study, granular ferric hydroxide was used as adsorbent for removal of hexavalent chromium. Besides, the effects of changing contact time, pH and concentrations of competitive anions were determined for different amounts of granular ferric hydroxide. It was found that granular ferric hydroxide has a high capacity for adsorption of hexavalent chromium from water at pH \leq 7 and in 90 min contact time. Maximum adsorption capacity was determined to be 0.788 mg Cr⁺⁶/g granular ferric hydroxide. Although relatively good adsorption of sulfate and chloride had been specified in this study, the interfering effects of these two anions had not been detected in concentrations of 200 and 400 mg/L. The adsorbability of hexavalent chromium by granular ferric hydroxide could be expressed by Freundlich isotherm with R²>0.968. However, the disadvantage was that the iron concentration in water was increased by the granular ferric hydroxide. Nevertheless, granular ferric hydroxide is a promising adsorbent for chromium removal, even in the presence of other interfering compounds, because granular ferric hydroxide treatment can easily be accomplished and removal of excess iron is a simple practice for conventional water treatment plants. Thus, this method could be regarded as a safe and convenient solution to the problem of chromium-polluted water resources.

Key words: Adsorption, hexavalent chromium, drinking water treatment, granular ferric hydroxide

INTRODUCTION

Chromium, priority metal pollutant, exists primarily in trivalent and hexavalent states in aquatic environment. The trivalent chromium is relatively non-toxic and in fact an essential trace nutrient in the human diet, but the hexavalent chromium is very toxic, being a mutagen and a potential carcinogen (Altundogan, 2005). Hexavalent chromium, which is primarily present in two forms of chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻), poses significantly higher levels of toxicity in comparison with other valence states (Sharma and Forester, 1995). As an example, US regulations have set the following limits for chromium discharges: 170 mg/L of Cr (III) and 0.050 mg/L

of Cr (VI) and the USEPA Drinking Water regulations limit the total chromium in drinking water to \leq 0.1 mg/L (Altundogan, 2005). Removal of Cr from certain contaminated resources remains an important issue in environmental remediation because of the mutagenic and carcinogenic characteristics of various chromium compounds (Nriagu and Nieboer, 1988).

Contamination of groundwater by Cr at numerous localities primarily is resulted from uncontrolled or accidental release of Cr-bearing solutions, used in various industrial applications, into the subsurface environment. Cr in such solutions mostly occurs as oxyacids and oxyanions of Cr (VI). Cr in this oxidation state is highly soluble, mobile and toxic (Mukhopadhyay *et al.*, 2007).

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Much research has focused on the remediation of Cr (VI) and many treatment processes have been developed. Physio-chemical adsorption has long been researched, but the cost is high and the Cr (VI) is just transferred but not removed. Chemical reduction-precipitation in which Cr (VI) is reduced to Cr (III) with subsequent precipitation of Cr (III) as chromic hydroxide ($\text{Cr}(\text{OH})_3$) is the most widely used method for removal of Cr (VI) from waste streams (Eckenfelder, 1989). The reducing agent in this process is chiefly a salt of either S (IV) or Fe (II). The method is a two-step process in which reduction and precipitation at highly acidic and alkaline pH conditions occur in succession. A variation of this method that emerged in the past decade is the reduction and precipitation of Cr (VI) from contaminated water stream in a single step by electrochemical addition of Fe (II). A formal description of this technology, the controlling factors, its metrics and limitations are lacking in the literature (Sengupta, 1995).

Granular ferric hydroxide (GFH) is an adsorbent, developed especially for arsenic removal from natural water. The adsorption process is reported to be a chemical reaction and anions other than arsenic may interfere in this process. This product was first manufactured at the Technical University of Berlin, Germany, Department of Water Quality Control, for selective removal of pollutants (Driehaus *et al.*, 1998). The objective of this project was to determine the effectiveness of this new adsorbent in removal of hexavalent chromium from drinking water.

MATERIALS AND METHODS

Preparation of the adsorbent

Granular ferric hydroxide (GFH) was purchased from a German company named Wasserchemie GmbH and Co. KG. The characteristics of this product are reported in Table 1. Before use, GFH was dehydrated in oven (105°C) for 90 min and placed in desiccators for cooling.

Preparation of water samples

Salt of chromium used for making synthetic water samples was analytical grade potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), and the required solution concentrations of this salt (0.5, 1 and 2 mg/L) were freshly prepared. Solutions of sulfate and

Table 1: Characteristics of GFH (according to the manufacturer)

Composition	100% Akaganeite ($\gamma\text{-FeOOH}$)
Specific surface area (m^2/g)	280
Particle size (mm)	0.32-2
Point of zero charge	pH 7.5...8.2
Water content (%)	43-48
Bulk density (kg/m^3)	1250
Porosity of grains (%)	72-77
Price (EUR/t)	4200

chloride (as competitive anions) were provided in two concentrations of 200 and 400 mg/L by use of their pure salts of them (potassium sulfate and sodium chloride). Deionized water was used for preparation of all these solutions. The experiments were accomplished in the Chemistry laboratory of Environmental Health Engineering Department in Tehran University of Medical Sciences.

Experimental procedure

For running the adsorption tests, the specified solution of hexavalent chromium was blended with GFH. The doses of GFH used in these tests were 0.25, 0.5, 1.0 and 1.5 g/L and mixing process (300 rpm) was accomplished by use of a shaker (model Heidolph). In this way, adsorption of Cr (VI) in the concentration range of 0.5, 1 and 2 mg/L was examined in different contact times of 5, 10, 15, 30, 60, 90 and 120 min, and in the end, detection of residual concentration of hexavalent chromium was accomplished by use of spectrophotometer (model DR2000). pH adjustment of water samples in the range of 5 to 8 was carried out by addition of 0.02 N nitric acid or 0.02 N sodium hydroxide solution and pH analysis was performed by a pH meter model E520. Development of adsorption isotherms for this study was done by exposing known concentrations of hexavalent chromium (0.25, 0.5, 1.0, 1.5, 2.0 and 3.0 mg/L) to a fixed dosage of adsorbent (5 g/L) in the pH of 7. These solutions as well as a blank were then allowed to equilibrate in a rotating apparatus at 300 rpm (at a constant temperature of 25°C). Finally, equation 1 was used for calculation of milligram hexavalent chromium adsorbed on one gram of adsorbent (qe):

$$qe = \frac{(C_o - C_e)V}{m} \quad (1)$$

Where:

- q_e = of mg adsorbed per gram of adsorbent , mg/g
- C_o = initial concentration of adsorbate, mg/L
- C_e = equilibrium concentration of adsorbate, mg/L
- V = volume of solution, L
- m = mass of adsorbent, g

In order to determine the effects of competitive anions, two concentrations of 200 and 400 mg/L for both sulfate and chloride as the most abundant anions present in natural waters were prepared and adsorption tests of hexavalent chromium (in three concentrations of 0.5, 1.0 and 2.0 mg/L and by using a dosage of 0.5 g of GFH) were repeated under the influence of these competing anions at the contact time of 90 min. Besides, the amount of iron added to water had been measured for both synthetic samples (with and without competitive anions) by use of a colorimetric method at the wavelength of 510 nm. Measurement of sulfate, chloride and iron had been done according to the producers described in Standard Methods (APHA, 2005). The model of visual spectrophotometer used for these analyses was PerkinElmer and before analyses, all of the water samples had been filtered by use of 0.45 μ m Wattman filter paper.

RESULTS

Fig. 1 shows the effects of changing contact time on adsorption of concentrations of 0.5 mg/L of hexavalent chromium by a fixed dosage of GFH. As presented in Fig. 2, the effects of changing contact time on adsorption of concentrations of 1 mg/L of hexavalent chromium by a fixed dosage of GFH can be seen. Fig. 3 demonstrate the effects of changing contact time on adsorption of concentrations of 2 mg/L of hexavalent chromium by a fixed dosage of GFH.

Effects of pH change on adsorption of hexavalent chromium in three different concentrations of 0.5, 1.0 and 2.0 mg/L at a constant contact time of 90 min can be seen in Fig. 4.

In Figs. 5 to 6, the results of developing adsorption isotherm for hexavalent chromium adsorption by GFH are presented.

Table 2 demonstrates the results of determining the effects of sulfate anion (SO_4^{-2}) on the process

of hexavalent chromium adsorption by 0.5 g/L GFH at the contact time of 90 min. Also Table 3 shows the results of determining the effects of chloride anion (Cl^-) on the process of hexavalent chromium adsorption by 0.5 g/L GFH at the contact time of 90 min. The amounts of iron added to water by this adsorbent with or without interfering anions can also be seen in these tables.

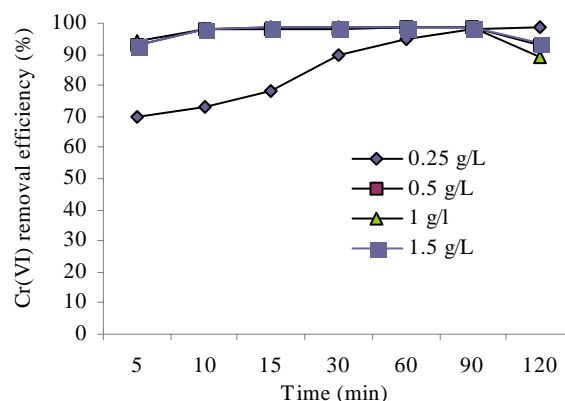


Fig. 1: Effect of contact time on removal efficiency of chromium (0.5 mg/L) by different amounts of GFH

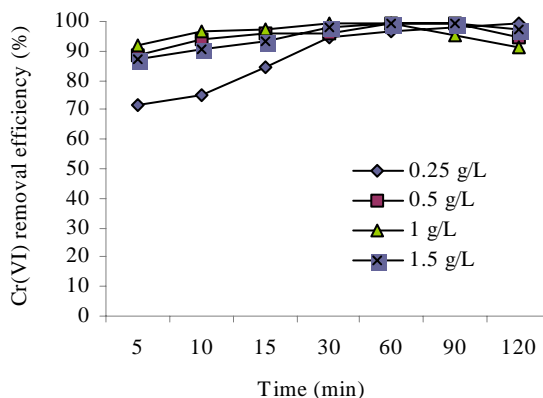


Fig. 2: Effect of contact time on removal efficiency of chromium (1 mg/L) by different amounts of GFH

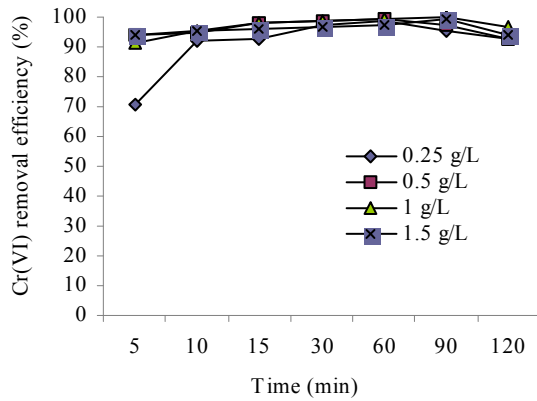


Fig. 3: Effect of contact time on removal efficiency of chromium (2 mg/L) by different amounts of GFH

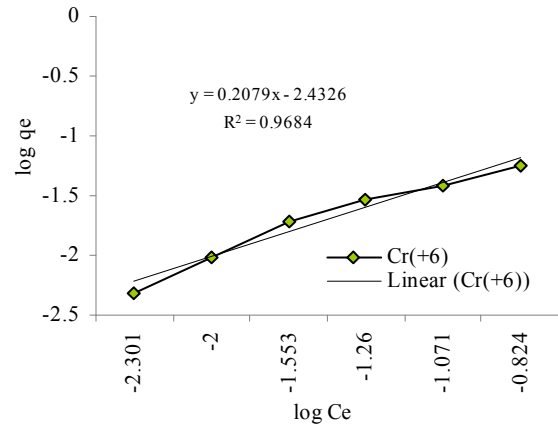


Fig. 5: Freundlich isotherm for adsorption of chromium by GFH

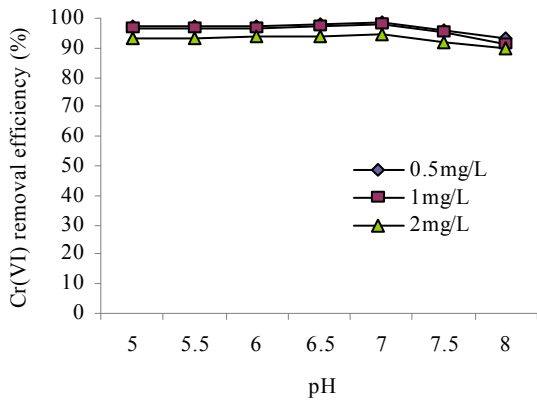


Fig. 4: Effect of pH on removal efficiency of chromium by GFH

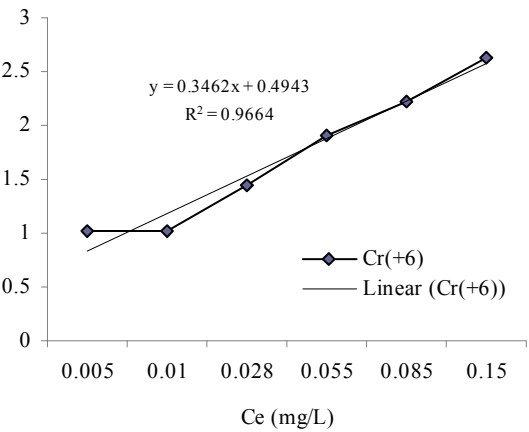


Fig. 6: Langmuir isotherm for absorption of chromium by GFH

Table 2: Effects of sulfate anion on chromium adsorption and resulted increase in iron concentration

Initial Cr(VI) conc. $\mu\text{g/L}$	Initial sulfate conc. mg/L	Residual Cr(VI) conc. $\mu\text{g/L}$	Residual Cr(VI) in the presence of sulfate $\mu\text{g/L}$	Residual sulfate conc. mg/L	Added iron conc. mg/L	Added iron conc. in the presence of sulfate mg/L
500	200	5	5	40.72	0.66	1.23
1000	200	15	13.5	45.83	0.45	1.16
2000	200	68	64	51.077	0.51	0.87
500	400	5	5	281.1	0.42	0.97
1000	400	15.5	14	306.72	0.65	0.79
2000	400	71.8	70.9	345.21	0.48	0.88

Table 3: Effects of chloride anion on chromium adsorption and resulted increase in iron concentration

Initial Cr(VI) conc. $\mu\text{g/L}$	Initial chloride conc. mg/L	Residual Cr(VI) conc. $\mu\text{g/L}$	Residual Cr(VI) in the presence of chloride $\mu\text{g/L}$	Residual chloride conc. mg/L	Added iron conc. mg/L	Added iron conc. in the presence of chloride mg/L
500	200	5	5	69.69	0.66	0.81
1000	200	15	16	57.177	0.45	0.39
2000	200	68	66.5	71.434	0.51	0.31
500	400	5	5	62.51	0.42	0.35
1000	400	15.5	14.7	87.56	0.65	0.56
2000	400	71.8	75.3	85.78	0.48	0.80

DISCUSSION

As shown in Figs. 1 to 3, the amounts of removal efficiency of hexavalent chromium were minimum in 5 min contact time for initial concentrations of 0.5, 1, and 2 mg/L, but these efficiencies were considerably increased at higher contact times and maximized at 90 min. Then, desorption of chromium had been occurred by further increasing the time. According to Figs. 1 to 3, it could be concluded that hexavalent chromium adsorption was enhanced by increase in adsorbent dosage. However, 0.5 g GFH/L of solution was sufficient to maximize this treatment. Since this study was innovative for chromium and there are no similar studies for chromium removal by GFH, these results is comparing with studies that were conducted for Arsenic. These results are in accordance to Bannerjee *et al.*, (2003) who obtained the optimized parameters for As treatment by GFH. (2003). Changes in pH, as shown in Fig. 4 was effective in adsorption process of hexavalent chromium such that at pH_s of equal to or less than 7, the removal efficiency was relatively high for all the three initial concentrations of hexavalent chromium but at higher pH_s the efficiencies of treatment had relatively reduced. The data from the study of Thriunavukkarasu *et al.*, (2003) also provided evidence that optimum pH for As removal by GFH was 7.6. Also, according to another research performed by Sperlich, *et al.*, (2005) the pH_s of 7-7.6 were specified to be as the optimum pH values for As adsorption by GFH. On the other hand, Banerjee, *et al.*, (2003) reported that at pH_s of more than 8.5, the efficiency of As adsorption by GFH had not changed whereas at pH values of less than 7.5, this efficiency had become significant.

By considering of correlation coefficients obtained from Ferundlich isotherm, it could be concluded that as shown in Figs. 5 and 6, the absorbability of hexavalent chromium may be expressed by this isotherm with R^2 value (>0.968). Furthermore, the Langmuir isotherm (R^2 value) that was obtained from this study was $R^2>0.966$. This result is not in accordance with the work of Badruzzaman, *et al.*, (2004) who reported the R^2 value of 0.92 for arsenate adsorption by GFH.

However, researches conducted by Sperlich, *et al.*, (2005) and Amy, *et al.*, (2004) showed that absorbability of arsenic by GFH at $pH=7$ could be described by both isotherms of Feroundligh and lungmoher and similar results are reported by Westerhoff, *et al.*, (2005) for As adsorption by GFH in $pH=7.5$.

Presence of sulfate and chloride ions had not significant effect on adsorption of Cr (VI) (see Tables 2 and 3) in spite of the fact that these anions had also been adsorbed by GFH. Results clearly showed that chloride initial concentrations of 200 and 400 mg/L had decreased to 57.177 and 62.51 mg/L when samples containing chromium were treated by GFH. Chloride reduction was slightly less in the presence of Cr (VI). However, the efficiency of chloride adsorption by GFH was more than sulfate and in other words interfering effect of sulfate for the process of Cr (VI) adsorption by GFH was less than chloride (residual amounts of chloride were much less than sulfate at the end of the equilibration periods).

Water treatment by GFH may increase the concentration of iron. In this study, the minimum and maximum amounts of iron added to water when Cr (VI) adsorption was accomplished in the presence of interfering anions of chloride and sulfate were 0.31-0.81 and 0.87-1.23, respectively. It seems, though that the increase in iron concentration would be less in the case of chloride presence. On the other hand, during Cr (VI) adsorption by GFH the minimum amounts of iron added to water was 0.42 mg/L and the maximum was 0.66. Thus, it could be concluded that the increase in iron concentration would be nearly the same when Cr (VI) adsorption is accomplished under the influence of either sulfate or chloride. Any how, the residual concentration of iron was more than the standard value set for drinking water (0.3 mg/L), but this should not be considered as a disadvantage since iron removal is not a complicated practice for conventional water treatment plants and indeed it is regularly accomplished (AWWA, 1999). Based on the results of this study, it could be declared that the adsorption capacity of GFH is high for Cr removal from drinking water even when the initial

concentration of Cr is relatively high. The optimum contact time for this treatment is estimated to be 90 min. It was indicated that the maximum adsorption capacity for Cr⁺⁶ was 0.788 mg Cr⁺⁶ per gram of GFH. Since the best treatment efficiency was observed in pH<7, which is in the pH range of natural water samples, there is no need to do pH adjustments. It is possible to improve the efficiency of treatment by increasing the GFH dosage, but this practice is not recommended because GFH is in fact quite efficient even in low doses of application.

A relatively good treatment is expected for chloride removal in water as well. But, the need to import this product from the foreign countries at a relatively high cost and the possible increase of iron concentration in water appear to be the main concerns in using GFH in Iran. Yet, it is feasible to make this product in any part of the country which has the problem of Cr in drinking water. Once the GFH has exhausted its adsorption capacity, it should be removed and replaced with new adsorbent because regeneration process has not economical justification and it may produce hazardous wastewaters. Exhausted GFH should be disposed in an approved landfill. Analysis of the used adsorbents by toxic characteristic leaching producer (TCLP) is recommended for forthcoming studies. A review work for introducing other cheap adsorbents of heavy metals from aqueous solutions (Mahvi, 2008) clearly shows that some waste products such as agricultural fibers could also be used for this purpose. But the treatment efficiency of these adsorbents are not as high as artificial adsorbents and with respect to adsorption of Cr⁺⁶ it is indeed low.

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